IR luminescence from the 1G_4 multiplet of Pr^{3+} in various doped crystals

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Abstract

Emission spectra, Stark component positions and fluorescence dynamics of the directly excited 1G_4 multiplet of Pr^{3+} in various oxide or fluoride crystals have been studied.

Introduction

The interest in the Stark component positions and lifetime of the 1G_4 multiplet of Pr^{3+} in doped materials is mainly due to the fact that the $^1G_4 \rightarrow ^3H_5$ fluorescence takes place at about $1.3\mu m$ in the transmission window of fibers and is usable for optical amplification and laser emission. Another interest is that pumping close to this level in the near IR may lead to blue ($^3P_0 \rightarrow ^3H_4$) or orange ($^1D_2 \rightarrow ^3H_4$ or $^3P_0 \rightarrow ^3H_6$) emissions by up-conversion to one of the 3P_J or 1I_6 manifolds [1]. However, few spectroscopic properties of the 1G_4 multiplet have been reported for crystals, less than in the case of glasses or fibers.

This paper compares the properties of the 1G_4 multiplet in several Pr^{3+} doped crystals : oxides, $Y_3Al_5O_{12}$ and $YAlO_3$, or fluorides, $LiYF_4$, BaY_2F_8 and LaF_3 .

Excitation and emission spectra

They have been recorded at 4.4K with a c.w. Ti:sapphire laser (resolution 2 GHz) pumped with an Ar laser (figures 1 and 2). Such spectra have never been published to our knowledge, contrary to the 3P_0 or 1D_2 ones. These experiments are in progress for LaF_3 .

The table 1 gives the position of the Stark components of the 1G_4 multiplet, which have been observed according to symmetry and selection rules. They have been verified with the help of the absorption spectra and the 3P_0 or 1D_2 emission spectra. They confirm and precise the literature data for $Y_3Al_5O_{12}$ [2] and $LiYF_4$ [3]. For $YAlO_3$ and BaY_2F_8 , the whole energy level scheme, completing previous reports [4], will be published elsewhere.

Figure 1: $^1\text{G}_4 \rightarrow ^3\text{H}_5$ unpolarized emission spectra at 4.4K

Figure 2: $^3\text{H}_4 \rightarrow ^1\text{G}_4$ excitation spectra at 4.4K

The table 2 gives the wavelengths of the most intense lines of the emission from 1G_4 to the lowest Stark components of 3H_5 . They are in agreement with the literature data on the 3H_5 Stark components. We have also recorded the weaker $^1G_4 \rightarrow ^3H_4$ spectra, which confirm the 3H_4 Stark splittings.

YAG	YAP	YLF	YBF
9712	9590	9699	9712
9823	9668	9831	9743
9833	9774	10113	9911
9852	9793	10129	9968
10114	10006	10313	10097
10127	10081	10426	10272
10261	10130	10474	10609
10284	10219	-	-
-	-	-	-

Table 1: 1G_4 observed energy levels (cm^{-1}).

YAG	YAP	YLF	YBF
1.3466	1.3433	1.3467	1.3363
1.3587	1.3598	1.3595	1.3382
	1.3613		1.3406
	1.3659		1.3485
	1.3682		

Table 2: Fluorescence line wavelengths (nm) related to the emission from 1G_4 to the lowest Stark components of the 3H_5 level.

1G_4 fluorescence decays

They have been recorded with a cooled Ge detector (response time $0.4\mu\text{s}$) on a Lecroy digital oscilloscope, when monitoring the most intense $^1G_4 \rightarrow ^3H_5$ emission after exciting into one of the 1G_4 Stark components with a YAG pumped, Raman-shifted, pulsed dye laser.

The room temperature and 12K decays are exponential over almost 3 decades, except for LiYF_4 . The experimental decay times (table 3) are compared to the radiative decay times, given in literature [14,15] or calculated in this work using published Judd-Offelt parameters [11-13].

It appears that the 1G_4 decays, in such low Pr^{3+} concentrated crystals, are dominated by multiphonon nonradiative relaxations, as the experimental decay times are clearly shorter than the calculated radiative lifetimes, the contributions of which are negligible, except for LaF_3 . Going down the table, from oxides to fluorides, the decay rate decreases in agreement with the increase of the number of phonons p involved in the nonradiative de-excitation and estimated as the ratio between the energy gap ΔE from the lower 1G_4 level to the higher 3F_4 level and the maximum phonon energy $\hbar\omega$. The experimental nonradiative decay rate W_{NR} , calculated with the formula $\tau_{\text{rad}}^{-1} = \tau_{\text{rad}}^{-1} + W_{\text{NR}}$, are compared to the values calculated with the empirical "gap law": $W_{\text{NR}}(0) = \beta \exp(-\alpha\Delta E)$ [17]. The evolution is coherent but the agreement between the numerical values is not always good, emphasizing, as often, the approximative character of the "gap law". It can be noticed that the ratio of the decay rates at R.T. and 12K is satisfactorily accounted for by the empirical formula $W_{\text{NR}}(T) = W_{\text{NR}}(0) [\exp(\hbar\omega / kT) / \exp(\hbar\omega / kT) - 1]^p$.

The behavior of LiYF₄ appears different from that of other crystals: the decays are not exponential, especially at low temperature. This can probably be explained by energy transfer and cross-relaxation, due to higher Pr³⁺ concentration. At room temperature the decay is less non-exponential than at 12K probably because of energy diffusion.

Crystal	[Pr ³⁺] (%)	$\tau_{\text{exp}}(\text{R.T.})$ (μs)	$\tau_{\text{exp}}(12\text{K})$ (μs)	¹ G ₄ - ³ F ₄ gap (cm ⁻¹)	Phonon energy (cm ⁻¹)	τ_{rad} (ms)	$W_{\text{NR}}^{\text{exp}}$ (s ⁻¹)	$W_{\text{NR}}^{\text{exp}}$ (s ⁻¹)
YAG	0.08	≈ 0.5	≈ 0.5	2222 [2]	865 [6]	0.92 [11]	2 10 ⁶	2.2 10 ⁶ [16]
YAP	0.1	0.86	0.86	2202	780 [7]	1.31 [12]	1.2 10 ⁶	2 10 ⁵ [17]
YLF	0.24	17	non expo.	2479 [3]	566 [8]	2.36 [13]	7.1 10 ⁴	2.8 10 ³ [17]
YBF	0.1	38	89	2465	415 [9]	2.29 [14]	1.08 10 ⁴	2 10 ³ [17]
LaF ₃	0.1	258	951	2547 [5]	350 [10]	3.1 [15]	730	250 [17]

Table 3: ¹G₄ fluorescence decay parameters.

Conclusion

Emission spectra and fluorescence dynamics of the directly excited ¹G₄ multiplet of Pr³⁺ in various, lightly doped, crystals have been studied. For all investigated systems, maximum of the ¹G₄→³H₅ emission is in the 1.35μm band. It was found that the ¹G₄ decay is mostly nonradiative, except for LaF₃, for which the radiative contribution is not negligible and may be affected by cross-relaxation at higher activator concentrations.

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